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(54) SECONDARY BATTERY AND POSITIVE ELECTRODE ACTIVE MATERIAL THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To improve capacity during low load and high load by containing a first conduction agent covering each particle surface of a number of metal oxides comprising a main body of an active substance, and a second conduction agent intervened between these particles, a specific surface area being smaller than a first conduction agent.

SOLUTION: As metal oxide comprising a main body of active positive electrode active material, lithium manganese oxide, lithium nickel oxide or the like can be employed. As a first conduction agent, Kechen black and acetylene black or the like whose specific area is 250 to 1500 m²/g can be employed. As a second conduction agent, carbon particles or the like whose specific area is 1 to 200 m²/g can be employed. The additive amount of the first conduction agent is preferably 0.5 wt.% or more and 5.0 wt.% or less to a metal oxide. In addition, a total additive amount of the first and second conduction agents is preferably 2.5 wt.% or more and 14.0 wt.% or less.

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CLAIMS

[Claim(s)]

[Claim 1] Positive active material of the rechargeable battery characterized by intervening between the particle of the metallic oxide of a large number which constitute the body of an active material, the 1st electric conduction agent which covers each particle front face of said metallic oxide, and each particle of said metallic oxide, and specific surface area containing the 2nd electric conduction agent smaller than said 1st electric conduction agent.

[Claim 2] Said addition Awt% [as opposed to / specific surface area is 250m² / g-1500m² / g, and / said metallic oxide] of 1st electric conduction agent is the positive active material of the following range, 0.5wt%≤A≤5.0wt%, and the rechargeable battery according to claim 1 that comes out and is characterized by a certain thing.

[Claim 3] Said 2nd electric conduction agent is the positive active material of the rechargeable battery according to claim 1 characterized by specific surface area being 1m² / g-200m² / g.

[Claim 4] Said metallic oxide A lithium manganic acid ghost, a lithium nickel oxide, It is what is chosen from at least one sort in a lithium cobalt oxide and manganese oxide. Said 1st electric conduction agent Specific surface area is 1000m² / g-1500m² / g. Said 2nd electric conduction agent The relation of the following [% / to said metallic oxide of addition Awt% / as opposed to / specific surface area is 1m² / g-25m² / g, and / said metallic oxide of said 1st electric conduction agent /, and both / said / the electric conduction agent / sum total addition Bwt], Positive active material of the rechargeable battery according to claim 1 characterized by a certain thing 0.5wt%≤A≤5.0wt% and 2.5wt%≤B≤14.0wt% at 0.5wt%≤B-A.

[Claim 5] Fine-particles resistance is 1.0×10². Claim 1 characterized by being below omega thru/or positive active material of the rechargeable battery of any one publication of four.

[Claim 6] The rechargeable battery characterized by having claim 1 thru/or the positive active material of any one publication of five.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a rechargeable battery and its positive active material.

[0002]

[Description of the Prior Art] Although various metallic oxides are used as positive active material of a rechargeable battery from before, since the electronic electric conductivity of the metallic oxide itself is low, the many have added the electric conduction agent which consists of carbon powder to a metallic oxide. By adding an electric conduction agent, electronic conductivity is given between each metallic oxides, and the reduction reaction is promoted.

[0003] Here, the mixed state of a metallic oxide and an electric conduction agent poses a problem as one of the causes which affects the cell engine performance. That is, metallic-oxide powder and carbon material impalpable powder are whether to be [how] in contact with homogeneity with sufficient frequency. If such contact reinforcement falls, since the part by which transfer supply of the electron is not fully carried out at positive active material will arise and the active material which remains as a result while it has been unreacted will arise, the utilization factor of positive active material falls.

[0004] As what solves the above-mentioned problem, the positive active material which formed graphite impalpable powder in the manganese-dioxide particle front face in the shape of a layer is proposed by JP,61-214362,A, and the positive active material which set the particle-size ratio of metallic-oxide powder and artificial-graphite powder to 10-1 to 10-5, and made coverage of a wrap carbon material 0.5 - 15% for the metallic oxide is proposed by JP,7-36332,B at it.

[0005] Moreover, the positive active material which becomes JP,9-92265,A from the positive active material with which wrap specific surface area consists 15% or more on the front face of appearance of a metallic oxide of a carbon material 150m² / more than g by the thickness of 0.01 micrometers - 0.3 micrometers, and the carbon powder which constitutes the electric conduction agent which intervenes between these positive active material is proposed.

[0006]

[Problem(s) to be Solved by the Invention] However, although the time of low loading and the utilization factor of positive active material good in the time of a load are shown in the rechargeable battery using the positive active material of each above-mentioned official report according to this invention person's etc. examination, it is usually current density 4.0 mA/cm², for example. It turned out that the time of the heavy load of extent of cell properties, such as capacity, is inadequate. This is presumed to be based on the following reasons.

[0007] That is, since metallic-oxide powder is covered with electric conduction agent powder, conductivity is equalized in the whole metallic oxide, therefore the utilization effectiveness of an active material shows a capacity good and high at low loading.

However, since an interface exists between the particles of each metallic-oxide powder, at the time of a heavy load, this is resisting, utilization effectiveness will fall and capacity will also become low.

[0008] Since a mass cell property is required with the time of low loading at the time of a heavy load when using a rechargeable battery for an electric vehicle etc., the improvement in the engine performance at the time of the heavy load of a rechargeable battery is indispensable. Then, this invention aims at offering the positive active material of the rechargeable battery which is compatible in a good capacity at the time of low loading and a heavy load in view of the point describing above.

[0009]

[Means for Solving the Problem] this invention person etc. noted supposing that a good capacity is maintained by improving utilization effectiveness of an active material above by covering the particle front face of metallic-oxide each with a coat electric conduction agent at the time of low loading, forming an electronic electric conduction path at the time of a heavy load by adding still more nearly another electric conduction agent (henceforth an addition electric conduction agent), and aiming at improvement in cell capacity. Moreover, it took into consideration also about the effect of electrode-izing on positive active material.

[0010] Usually, the coat of the metallic oxide by the electric conduction agent is performed using the method of the so-called mechano processing (mechano fusion) of mixing both with mechanical energies, such as compression and shearing, and carrying out surface fusion of two or more particles. In the coat by mechano processing, a coat electric conduction agent needs to be a particle (namely, particle with a large specific surface area) smaller than an active material particle more than fixed [a certain].

[0011] this invention person etc. considered the coat by this mechano processing. The result is shown in drawing 3 . Drawing 3 shows transition of the specific surface area of the (mixed powder) of the metallic-oxide particle after being covered with the coat electric conduction agent to the coat electric conduction agent addition (as shown for example, all over drawing, it is 0.5wt(s)% - 5.5wt%) to a metallic oxide. Here, the processing time of an axis of abscissa is the time amount which the above-mentioned mixing took.

[0012] The reduction is saturated with a certain time amount although the specific surface area of the electric conduction agent after a coat decreases with the processing time. Moreover, the specific surface area of the electric conduction agent after a coat also increases with the increment in a coat electric conduction agent addition. In electrode-izing of the covered metallic oxide, although each particle is combined with a binder and the positive electrode was constituted, as for this invention person etc., the coat electric conduction agent addition found out that the specific surface area of the electric conduction agent after a coat is excessive (it is size for example, from 40m²/g), and the thing which it becomes, and peeling, a chip, etc. produce and burn of an electrode and to become above a certain extent (it is size for example, from 5wt%). Here, although what is necessary is just to increase the amount of binders, the part cell capacity falls.

[0013] Therefore, when it is the same as a coat electric conduction agent, or specific surface area of the above-mentioned addition electric conduction agent was made larger than it and an addition electric conduction agent is added, a possibility that it may become the same as having made the addition of a coat electric conduction agent increase

substantially, the fault size of the specific surface area of the electric conduction agent after the above-mentioned coat may be produced, and the above-mentioned peeling, a chip, etc. may arise in an electrode is. Therefore, as for an addition electric conduction agent, for electrode-izing, it is desirable that specific surface area is smaller than a coat electric conduction agent. Moreover, it is thought that particle size of an addition electric conduction agent can be enlarged, and it intervenes between metallic-oxide particles by making specific surface area of an addition electric conduction agent larger than a coat electric conduction agent, and becomes easy to form an electronic electric conduction path.

[0014] And based on the above-mentioned examination result, it came to adopt the following technical means. That is, according to invention according to claim 1, it is characterized by intervening between the particle of the metallic oxide of a large number which constitute the body of an active material, the 1st electric conduction agent which covers each particle front face of a metallic oxide, and each particle of a metallic oxide, and specific surface area containing the 2nd electric conduction agent smaller than the 1st electric conduction agent.

[0015] While capacity at the time of low loading is made by the 1st electric conduction agent as it is good, since an electronic electric conduction path is secured by the 2nd electric conduction agent which intervenes between metallic-oxide particles at the time of a heavy load and the active material (metallic oxide) of the circumference of it is used by it by it, improvement in utilization effectiveness can be aimed at and good capacity can be realized by it. Furthermore, since specific surface area is smaller than the 1st electric conduction agent, excessive prevention of the specific surface area of the electric conduction agent after a coat is made, and the 2nd electric conduction agent can prevent peeling, a chip, etc. in electrode-izing.

[0016] therefore -- while it is compatible in a good capacity at the time of low loading and a heavy load according to this invention -- good -- an electrode -- the positive active material of the rechargeable battery [-izing / a rechargeable battery] can be offered. Here, the 1st electric conduction agent is considered that the specific surface area has the suitable range from problems, such as peeling in mechano processing and electrode-izing, as mentioned above.

[0017] Moreover, about the 2nd electric conduction agent, when the specific surface area is too smaller than the 1st electric conduction agent, that the particle diameter of volume which will become large and is occupied in positive active material increases, for example, the amount of an active material becomes less, and capacity falls etc. has bad effectiveness. The 2nd electric conduction agent should just be the magnitude which can secure an electronic electric conduction path. Therefore, it is thought that the specific surface area has the suitable range also about the 2nd electric conduction agent.

[0018] In view of the point describing above, the experiment was able to be repeated further wholeheartedly about different various electric conduction agents, such as various metallic oxides and configurations, and construction material, and it was able to ask about the specific surface area and the addition of a suitable electric conduction agent to do so the effect of the invention of the claim 1 above-mentioned publication. And we decided to adopt claim 2 thru/or invention according to claim 4. That is, according to invention according to claim 2, the 1st electric conduction agent is characterized by addition Awt% [as opposed to a metallic oxide in specific surface area] being

0.5wt% $\leq A \leq$ 5.0wt% by 250m² / g-1500m² / g. Moreover, according to invention according to claim 3, the 2nd electric conduction agent is characterized by specific surface area being 1m² / g-200m² / g.

[0019] According to invention according to claim 4, furthermore, a metallic oxide It is what is chosen from at least one sort in a lithium manganic acid ghost, a lithium nickel oxide, lithium cobalt oxide, and manganese oxide. The 1st electric conduction agent Specific surface area is 1000m² / g-1500m² / g. Said 2nd electric conduction agent Specific surface area is 1m² / g-25m² / g, and when the addition of the addition [of the 1st / to said metallic oxide of the 1st electric conduction agent / electric conduction agent], 1st, and 2nd electric conduction agents is made into Awt% and Bwt%, respectively It is characterized by having the relation of 0.5wt% $\leq B-A^{**}$

0.5wt% $\leq A \leq$ 5.0wt% and 2.5wt% $\leq B \leq$ 14.0wt%.

[0020] According to these claims 2 thru/or invention according to claim 4, while being stabilized more and being able to realize effectiveness equivalent to invention of the claim 1 above-mentioned publication, electrode-ization of positive active material can be performed good. Moreover, when the relation of the fine-particles resistance and the load characteristic of positive active material was investigated, the fine-particles resistance is 1.0x10² like invention according to claim 5. When it was below omega, it turned out that effectiveness equivalent to invention of the claim 1 above-mentioned publication is realizable.

[0021] Moreover, the rechargeable battery which both has positive electrodes which are compatible in a good capacity like invention according to claim 6 at the time of the rechargeable battery equipped with claim 1 thru/or the positive active material of any one publication of five then low loading, and a heavy load, and which are hard to generate, such as peeling and a chip, can be offered.

[0022]

[Embodiment of the Invention] Hereafter, this operation gestalt describes what was used as Li rechargeable battery as a rechargeable battery. With this operation gestalt, a lithium manganic acid ghost, a lithium nickel oxide, lithium cobalt oxide, manganese oxide, etc. can be used as a metallic oxide which constitutes the body of positive active material.

[0023] Each particle front face of a metallic oxide can be covered, and KETCHIE en black, acetylene black, etc. whose specific surface area is 250m² / g-1500m² / g can be used as a coat electric conduction agent (1st electric conduction agent) which equalizes electronic conductivity in a metallic oxide. In addition, in order to improve capacity more, it is more desirable that specific surface area is 1000m² / g-1500m² / g (refer to drawing 4 of JP,9-92265,A).

[0024] Moreover, it is further added to the covered metallic oxide, and the carbon powder whose specific surface area is 1m² / g-200m²/g as an addition electric conduction agent (2nd electric conduction agent) with a specific surface area smaller than a coat electric conduction agent (1st electric conduction agent) which intervenes between each particle of a metallic oxide and forms an electronic electric conduction path can be used. In addition, for improvement in an electrode consistency, it is more desirable that specific surface area is 1m² / g-25m² / g grade.

[0025] LiMn 2O₄ (mean particle diameter of 7 micrometers) is hereafter used as a metallic oxide as an example of positive active material. As a coat electric conduction agent, 0.03 micrometers of mean diameters, the LION KETCHIE en black of specific

surface area of $1270 \text{ m}^2 / \text{g}$ (it abbreviates to KB hereafter) -- using -- as an addition electric conduction agent -- the product made from RONZAJAPAN -- KS-6 (mean particle diameter of 3.4 micrometers, specific surface area of $21.3 \text{ m}^2 / \text{g}$), and company make -- the thing using KS-15 (mean particle diameter of 7.5 micrometers, specific surface area of $12.8 \text{ m}^2 / \text{g}$) is described. This operation gestalt is not limited to this example.

[0026] LiMn 2O_4 The mechano processing which covers KB on each particle front face is LiMn 2O_4 . Mixed powder which mixed KB of the specified quantity was performed using the coat formation equipment shown in drawing 1. This coat formation equipment consists of the 1st arm 4 with the press shearing head 3 of the semicircle configuration prolonged even near the inner skin of the rotating drum 1 with a building envelope 10, and the rotating drum 1 fixed to the fixed shaft 2 of this rotating-drum 1 interior, and the 2nd arm 6 with the pawl 5 which separates a predetermined include angle behind [revolution] this 1st arm 4, is fixed to the fixed shaft 2, and is prolonged even near the inner skin of a rotating drum 1.

[0027] It is LiMn 2O_4 by putting the above-mentioned mixed powder into the building envelope of this coat formation equipment, carrying out the predetermined time (processing time) revolution of the rotating drum 1 at a predetermined rotational frequency, applying press shearing force between the inner skin of a rotating drum 1, and the press shearing head 3, failing to scratch and mixing by the pawl 5, after that. KB was covered on each particle front face. LiMn 2O_4 covered with KB obtained by the above mechano processing With PVDF (polyvinylidene fluoride) which is a binder about KS-6 or KS-15, in addition, solvents (N-methyl-2-pyrrolidone etc.) were added and kneaded further, and it considered as the shape of a paste. Here, the binder was made into several % (for example, about 3%).

[0028] With the doctor blade method, the obtained paste was coated on aluminum foil charge collector, desiccation and press forming were performed after that, and the electrode (positive electrode) was created. This electrode was pierced to disc-like, the vacuum drying was carried out further, it carried in all over the dry box after that, and the coin mold cell was manufactured. the solvent which did Tonen Chemical TAPIRUSU25micrometer at Osaka Gas MCMB (mesophase carbon micro bead) and a separator, and did each 50 capacity % mixing of LiPF₆ of M6 / 1EC(50) DME (50), i.e., EC (ethylene carbonate) and DME (dimethoxyethane), at the counter electrode (negative electrode) at the electrolytic solution -- LiPF₆ The electrolytic solution which 1-M-dissolved was used.

[0029] Charge is the conditions of $4.2\text{V} \times 5\text{h}$, $1.0 \text{ mA}/\text{cm}^2$, and CC/valve flow coefficient, and discharge set assessment conditions to 3.0 V cuts and CC. To the table of drawing 2, it is discharge current consistency $4.0 \text{ mA}/\text{cm}^2$. The positive-electrode capacity factor (henceforth a capacity factor) in the various positive active material of this example of a case, at i.e., the time of a heavy load, is shown. the graph of drawing 2 -- LiMn 2O_4 A capacity factor is shown about what changed various all electric conduction doses (each wt%) when adding the receiving amount of KB, KS-15, or KS-6. Here, the above-mentioned amount of KB corresponds to addition Awt% to the metallic oxide of a coat electric conduction agent (1st electric conduction agent), and all the above-mentioned electric conduction doses correspond to sum total addition Bwt% to the metallic oxide of both the electric conduction agent.

[0030] The above-mentioned amount of KB is LiMn_2O_4 . It is the amount of KB when making total with an amount and the amount of KB into 100wt(s)%, and is indicated in the leftmost train in a graph as 4.0wt% 3.5wt% 2.5wt% 1.5wt% 0.5wt% 0wt%. moreover, all the above-mentioned electric conduction doses -- LiMn_2O_4 It is the sum total addition of the amount of KB and KS-15 amount (or KS-6 amount) when making total with an amount, the amount of KB, KS-15 amount (or KS-6 amount), and a binder (PVDF) into 100wt(s)%, and even 1.5wt(s)% - 10.0wt% is looked like [the maximum upper case in a graph], and it is shown in it.

[0031] here -- a capacity factor -- the amount of KB -- 0wt%, KS-15, or KS-6 -- 10wt(s)% -- since the capacity when adding was a good capacity, the capacity at this time has been shown as 1. And as for the capacity factor in the case (that is, KS-15 amount 1.0wt(s)%) of being 2.5wt(s)%, the amount of KB is expressed for the 1.5wt(s)% and all electric conduction dose as 1.04, for example. As for what [what shows a good capacity from this graph] (value surrounded with the broken line among drawing 2), i.e., the thing used as one or more capacity factors, it turns out that $2.5\text{wt}\% \leq B$ and value $B-A$ which deducted the amount of KB (A) from all electric conduction doses (B) further become [the amount of KB (A) / $0.5\text{wt}\% \leq A$ and all electric conduction doses (B)] a $B-A \geq 0.5\text{wt}\%$ thing. Incidentally, when there were few amounts of $B-A < 0.5\text{wt}\%$ of case, KS-15 [i.e.,], or KS-6, a good capacity factor was not obtained.

[0032] Moreover, when capacity is investigated also about the time of low loading (0.5 mA/cm²), it is LiMn_2O_4 that the total quantity of a coat and an addition electric conduction agent is more than 15wt%. In order that an amount might fall and the capacity at the time of low loading might decrease, it turned out that it is not desirable. Therefore, as for the total quantity (all electric conduction dose Bwt%) of a coat and an addition electric conduction agent, considering as $2.5\text{wt}\% \leq B \leq 14.0\text{wt}\%$ is desirable.

[0033] Moreover, as shown in drawing 3 stated in the column of a solution means, for electrode-izing, it is desirable for the addition of a coat electric conduction agent (coat electric conduction agent), i.e., KB, to be less than [5.0wt%]. In addition, the processing time of an axis of abscissa is the above-mentioned mechano processing time (unit: minute) among drawing 3 , and an axis of ordinate is LiMn_2O_4 . It is the specific surface area (unit: m² / g) of the mixed powder after covering KB, and each plot mark corresponds to each addition of KB. And if the addition of KB is larger than 5.0wt(s)%, since specific surface area will become larger than 40m² / g, peeling, a chip, etc. arise and come to be jealous of an electrode.

[0034] If based on the knowledge about the addition of each [these] electric conduction agent, the following can say. That is, about KB (coat electric conduction agent), it is LiMn_2O_4 . It is desirable that the receiving addition (amount Awt% of KB) is $0.5\text{wt}\% \leq A \leq 5.0\text{wt}\%$, and it is desirable that the sum total addition (all electric conduction dose Bwt%) of a coat and an addition electric conduction agent is $2.5\text{wt}\% \leq B \leq 14.0\text{wt}\%$.

[0035] Thus, the particle of the metallic oxide of a large number which constitute the body of an active material as positive active material, The coat electric conduction agent which covers each particle front face of a metallic oxide, and equalizes electronic conductivity in a metallic oxide, By having used the thing containing an addition electric conduction agent with a specific surface area smaller than a coat electric conduction agent which intervenes between each particle of a metallic oxide and forms an electronic

electric conduction path at the time of a heavy load while it is compatible in a good capacity at the time of low loading and a heavy load -- good -- an electrode -- the positive active material of Li rechargeable battery [-izing / rechargeable battery] can be offered. [0036] Here, a mechanism compatible in a good capacity at the time of low loading and a heavy load can be presumed to be as follows. It states with reference to the operation explanatory view of the electric conduction agent in the positive electrode of drawing 4 . Among drawing 4 , in an addition electric conduction agent and 21, a coat electric conduction agent and 22 show a positive-active-material particle (henceforth an active material), and 23 shows [20] a charge collector. And (a) is the case where a coat and the addition electric conduction agent 20, and 21 both are contained in an active material 22 by (c) when only the addition electric conduction agent 20 is contained in an active material 22, and, as for (b), only the coat electric conduction agent 21 is contained in an active material 22.

[0037] By the time of low loading, with the electrode of (a), since many clearances exist between active materials 22, there is an active material 22 which has not taken conductivity and capacity does not fully come out. In the electrode of (b), since conductivity can be taken to homogeneity by the coat electric conduction agent 21, capacity becomes [the utilization effectiveness of an active material 22] good highly. By the time of a heavy load, with the electrode of (a), since the addition electric conduction agent 20 is carrying out localization, the conductive electric conduction path of a good electron is formed very much in the part, and the active material 22 of the near is used. Therefore, capacity becomes high. With the electrode of (b), since an interface exists between each active materials 22, these interfaces are resisting, utilization effectiveness falls, and it is thought that capacity becomes low.

[0038] On the other hand, with the electrode of (c), since it is the combination of the electrode of the above (a) and (b), utilization effectiveness of an active material 22 can be enlarged at the time of low loading and a heavy load, and it can be compatible in a good capacity. By the way, about each positive active material into which the compounding ratio of the graph of above-mentioned drawing 2 was changed, when fine-particles resistance was investigated, the result as shown in drawing 5 was obtained.

[0039] Drawing 5 is a graph which shows the relation between the coat in positive active material, and the sum total addition (sum total electric conduction dose) of an addition electric conduction agent and fine-particles resistance of positive active material. Fine-particles resistance (omega) is shown on the axis of ordinate. Moreover, although the axis of abscissa is made into the sum total electric conduction dose (wt%), it has divided into 6.5wt% four case perpendicularly by the dotted line 4.5wt% 2.5wt% 10.0wt(s)% sequentially from the left.

[0040] And in the field of each sum total electric conduction dose, the numeric value shown in the graph is the amount of KB (wt%), and it is plotted from the left to the right in order so that it may increase from what has the few amount of KB. In addition, the plot of a sum total electric conduction dose 10.0wt% field is amount of KB 0wt%, mechano [i.e.,], a non-processed thing. Moreover, that in which, as for **, KS-6 and KB are contained, and <> show among drawing that in which KS-15 and KB are contained. It follows, for example, sets to a sum total electric conduction dose 6.5wt% field, and, for leftmost **, fine-particles resistance is about 1.0×10^2 . Although it is omega, as for this, KB is 0.5wt(s)% and KS-6 are 6.0wt(s)%.

[0041] For what shows a good capacity in the graph of drawing 2 from drawing 5 , fine-particles resistance is 1.0×10^2 . It turns out that it is in the field which becomes below omega. If it puts in another way, fine-particles resistance will be 1.0×10^2 . With omega [below], the load characteristic is improving. Since the electronic conductivity of an active material improved, this is considered. As mentioned above, although this operation gestalt has been described based on the above-mentioned example, if it is each metallic oxide described above in this operation gestalt, a coat electric conduction agent, and an addition electric conduction agent, effectiveness equivalent to this example can be acquired.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the outline sectional view showing the configuration of the coat formation equipment concerning the operation gestalt of this invention.

[Drawing 2] It is the graph showing the capacity factor to the various additions in the electric conduction agent in positive active material.

[Drawing 3] It is the graph which shows transition of the specific surface area of the mixed powder after the coat to the coat electric conduction agent addition to the metallic oxide in mechano processing.

[Drawing 4] It is the explanatory view showing an operation of the electric conduction agent in a positive electrode.

[Drawing 5] It is the graph which shows the relation between the addition of an electric conduction agent, and fine-particles resistance of positive active material.

[Description of Notations]

1 [-- The 1st arm, 5 / -- A pawl, 6 / -- The 2nd arm, 10 / -- A building envelope, 20 / -- An addition electric conduction agent, 21 / -- A coat electric conduction agent, 22 / -- A positive-active-material particle, 23 / -- Charge collector.] -- A rotating drum, 2 -- A fixed shaft, 3 -- A press shearing head, 4
